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## (57) Abstract

The invention relates to a coated component, in particular a coated tool for machining, having a substrate and a first carbon layer, which is applied to the substrate and has a predetermined fraction of carbon with a diamond crystal structure. There is the problem with such a component that the adhesive strength of the first carbon layer on the substrate is unsatisfactory in many instances. This problem is solved by virtue of the fact that provision is made of a second carbon layer, which is arranged further outside with reference to the substrate than the first carbon layer, and in the case of which the fraction of carbon with a diamond crystal structure is lower than the predetermined fraction of carbon with a crystal diamond structure in the first carbon layer. The invention also relates to a process for producing such a coated component.

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# Diamond-coated Tool and Process for Producing thereof

5 The invention relates to a coated tool, in particular for machining, according to the preamble of Claim 1, and to a process for producing such a tool.

10 To date, CVD processes have been used to produce these coated tools, which are also denoted as diamond-coated. As substrate materials, in particular for high-performance tools for forming in cutting and non-cutting fashions work-pieces which are to be processed, use is made of cemented carbide or cermet materials which are provided with a dia-  
15 mond layer with the aid of one of the said processes. These substrate materials consist, for example, of carbides to which nitrides or the like can be added, and which are embedded in a metal matrix, typically cobalt and/or nickel and/or iron. A known example is tungsten carbide with 0.2 to  
20 20% by weight of cobalt.

In the customary processes for applying diamond layers to substrates, it frequently happens that in conventional diamond layers instances of chipping occur which prevent  
25 further use of the tool in many cases.

The service life of conventional tools with diamond coatings is therefore substantially reduced because of instances of chipping.

30

EP 0279898 B1 discloses a process for applying an antiwear layer in the manner of a diamond film to a carrier, there being applied sequentially to the carrier a multiplicity of layers which in each case have a higher diamond fraction and  
35 a higher modulus of elasticity than the layer therebelow. In

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accordance with the disclosure of this printed publication, an attempt is made to use a flat gradient for the modulus of elasticity from the carrier up to the external diamond layers to prevent chipping of the layers. However, this process is very expensive in view of the number of process steps to be carried out. Moreover, the process has not always led to satisfactory results in the presence of stress through wear.

A diamond-coated component and a process for producing it are disclosed in EP 0752293 A2. This printed publication discloses firstly applying a carbon layer with a low diamond fraction to a carrier, after which a carbon layer with a higher diamond fraction is deposited. This process can be repeated a few times.

The design of a cutting bit for the edge of a tool is disclosed in US 5139372. In concrete terms, the printed publication describes the deposition of carbon/diamond double layers, the first step being to deposit a mixed layer with a high fraction of polycrystalline diamond on an  $\text{SiO}_2$  auxiliary or intermediate carrier, followed by a layer with a low fraction of polycrystalline diamond. Subsequently, the intermediate carrier is removed by etching and, in accordance with the invention described in the printed publication, fastened on a tool substrate by soldering with the aid of the "lower-concentration" diamond layer. Consequently, when the tool is finished the diamond layer with a higher diamond fraction is on the exposed side of the cutting bit. Moreover, this printed publication describes a comparative example in which the exposed side of the cutting bit on the finished tool has a carbon layer with a lower diamond fraction, and the carbon layer connected by soldering to the tool substrate has a higher fraction of diamond. Comparative trials likewise described in this printed publication show that those tools for which the exposed side of the cutting

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bit is formed by a carbon layer with a lower diamond fraction return substantially poorer results by comparison with the inverted layer sequence.

- 5 Starting herefrom, it is the object of the invention to create a coated tool having a substrate and a carbon layer, applied to the substrate, with carbon in a diamond crystal structure, in the case of which tool the risk of instances of chipping of the carbon layer are effectively reduced.
- 10 Moreover, the aim is also to specify a process for producing such a tool.

The object is achieved by means of a tool having the features of Claim 1. In context with the invention, the expression "tool" includes each component having a coating serving for abrasion resistance of the component. Examples of such a tool are cutting tools like mills, drills, twist drills, reamers, threaders, grinding tools, trueing tools and honing tools, forming / shaping tools like drawing tools, stamping tools and punching tools, and components of the above-mentioned kind like wear parts, fairlead bushes, lands, guide surfaces, slide faces, slide bearings and cutting faces. The most prominent examples are guide surfaces of twist drills, guide surfaces of reamers and cutting surfaces of inserts.

25 The last-mentioned examples refer to the fact that in most tools the cutting components are combined with sliding surfaces defining the position of the blade, such that components are integral with the tool. In this connection, the smooth diamond layers are particularly advantageous, because they have a high hardness and a low coefficient of friction.

30 The components may be mounted to a tool or made up by certain tool surfaces. In many cases, the tool coating includes a tool edge.

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The fraction of carbon with a diamond crystal structure is preferably very high in the first carbon layer, for example in accordance with previously used diamond coatings in the case of tools for machining workpieces. It has surprisingly  
5 been established that in the case when, by contrast with the first carbon layer, the second carbon layer has a smaller fraction of carbon with a diamond crystal structure, the formation of cracks in the carbon layer can be effectively reduced overall, with the result that instances of chipping  
10 occur very much more rarely.

In principle, both the first and the second carbon layer contain a highly predominant carbon fraction in diamond crystal structure (80-100%). These layers are mostly denoted  
15 in the literature as diamond layers. The remaining carbon is graphite or amorphous phases.

It is conjectured that the different coefficients of thermal expansion of the first and second carbon layers contribute  
20 to a reduction in the formation of cracks. Since, by contrast with the first carbon layer, the fractions of carbon with a graphite crystal structure and amorphous structure are increased in the second carbon layer, the coefficient of thermal expansion is also increased by contrast with the  
25 first carbon layer. The second carbon layer can include or consist of nano-crystalline diamond typically being surrounded by carbon of non-diamond structure. The last-mentioned carbon serves to increase the thermal extension coefficient of the second carbon layer. The generation of nano-  
30 chrystalline diamond films on substrates is, e.g. described in "Nucleation, Growth and Micro-Structure of Nano-Chrystalline Diamond Films" in "MRS Bulletin-Publication of the Materials Research Society", September 1998, Vol. 23, No. 9, p. 32-33, of Dieter M. Gruen. The contents of this citation  
35 is incorporated herein by reference.

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It is assumed that the above-mentioned values of the thermal extension coefficient in the substrate, the first and the second carbon layer can have the following effects:

- 5 The first carbon layer is, as known in the prior art, deposited at a substrate temperature  $> 600^{\circ}\text{C}$ , after which the finished component is cooled. Since the coefficient of thermal expansion of customary substrate materials is approximately a multiple greater than that of carbon with a diamond  
10 crystal structure (for example, approximately 5-fold for cemented carbide), a compressive stress is produced in the first carbon layer. By applying the second carbon layer with a coefficient of thermal expansion which is increased by comparison with the first carbon layer, the second carbon  
15 layer can exert an additional compressive stress on the first carbon layer, with the result that instances of chipping are avoided to the greatest possible extent. In particular, owing to the different stress states in the first and second carbon layers, it is possible, for example, for  
20 cracks occurring in the case of a coated material to be kept in the second carbon layer, and the tips of the cracks can no longer reach the substrate. In the context of this description, stress characteristics always refer to the direction parallel to the interface(s) of the carbon layers.  
25 Generally, the compressive stress should increase with decreasing distance from the substrate.

A further advantage of the coated component consists in that the ductility and smoothness of the second carbon layer  
30 likewise contributes to cracks being produced more rarely.

Moreover, when the coated component is used for machining the cutting forces and the tendency to smearing of material are less because the smoothness of the second carbon layer  
35 is increased by contrast with the smoothness of the carbon

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layer customarily used as outermost layer. This results in service lives which are likewise improved, while a higher quality of the surface of the processed workpiece, in particular its smoothness, is also achieved.

5

In addition to the first and second carbon layers, the coated tool can also have further material layers, the term "substrate" used here requiring to be understood as the material situated below the first carbon layer. It is also possible for further material layers to be arranged between the first carbon layer and the second carbon layer or beyond the second carbon layer with reference to the substrate. It is essential that from inside to outside with reference to the substrate there is firstly a carbon layer having a predetermined fraction of carbon with a diamond crystal structure, while the second carbon layer follows further on the outside.

The second carbon layer can be applied directly to the first carbon layer. Very good results have been returned with this embodiment as regards the adhesive strength of the carbon layers and their resistance to cracks.

However, it is likewise possible that formed between the first carbon layer and the second carbon layer is an inter-layer in the case of which the fraction of carbon with a diamond crystal structure drops continuously from the first carbon layer in the direction of the second carbon layer. This embodiment differs from the preceding embodiment explained essentially in that the transition in the fraction of carbon with a crystal diamond structure does not occur abruptly but extends over space.

The tool preferably has an overall thickness of the first carbon layer and of the second carbon layer in the range of



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1 to 40  $\mu\text{m}$ , the value ranges of 4 to 20  $\mu\text{m}$  and 6 to 15  $\mu\text{m}$  respectively leading to increasingly better results for the adhesive strength of the carbon layers.

- 5 The ratio of the thickness of the first carbon layer to the thickness of the second carbon layer can be in the range of 0.05 to 0.9, while a range of from 0.1 to 0.5 is to be regarded as preferred for this ratio.
- 10 The first carbon layer preferably has a structure such that upon irradiation by laser light at a wavelength of 514 nm (emission line of the Ar ion laser) the first carbon layer generates a Raman spectrum in the case of which, after subtraction of a signal background, the intensity ratio  $K_A$  of a
- 15 peak S, representative of carbon with a diamond crystal structure, at  $1332\text{ cm}^{-1}$  to a peak F, representative of carbon lacking a diamond crystal structure, at  $1560\text{ cm}^{-1}$  is in the range of from  $\infty$  to 0.5, in which case  $K_A = I(S_A)/I(F_A)$  is the diamond value for the first carbon layer.
- 20 The intensity ratio  $K_A$  of the peak S, representative of carbon with a diamond crystal structure, at  $1332\text{ cm}^{-1}$  to the peak F, representative of carbon lacking a diamond crystal structure, at  $1560\text{ cm}^{-1}$  is, further, preferably in the range
- 25 of from 10 to 1.0 which, for the ratio of the fractions of carbon with a diamond crystal structure to carbon of a different, for example graphitic or amorphous structure, has proved to be particularly favourable for the first carbon layer.
- 30 The second carbon layer preferably has a structure such that upon irradiation by laser light at a wavelength of 514 nm the second carbon layer generates a Raman spectrum in the case of which, after subtraction of a signal background, the
- 35 intensity ratio  $K_B$  of a peak S, representative of carbon with

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a diamond crystal structure, at  $1332\text{ cm}^{-1}$  to the peak F, representative of carbon lacking a diamond crystal structure, at  $1560\text{ cm}^{-1}$  is in the range of from 2 to 0, in which case  $K_s = I(S_A)/I(F_A)$  is the diamond value for the second carbon layer.

The intensity ratio  $K_s$  of the peak S, representative of carbon with a diamond crystal structure, at  $1332\text{ cm}^{-1}$  to the peak F, representative of carbon lacking a diamond crystal structure, at  $1560\text{ cm}^{-1}$  is, further, preferably in the range of from 1 to 0.1.

The secondary condition applies to all the abovenamed data on ranges in that the fraction of carbon with a diamond crystal structure in the second carbon layer is lower than the fraction of carbon with a crystal diamond structure in the first carbon layer, that is to say  $K_A > K_s$ . It is also possible in principle that in the case of the first carbon layer the peak F, and in the case of the second carbon layer the peak S is respectively completely missing in the Raman spectrum.

The second carbon layer preferably has a minimum thickness of  $0.5\text{ }\mu\text{m}$ , something which marks it off from effects which occur at the end of a conventional CVD diamond coating process and in the case of which a structure lacking diamonds can occur which cannot be denoted as a layer in the sense of this description and comprises a few layers of atoms. What is decisive, however, is that the thickness of the second carbon layer is selected in such a way that there is an adhesivity of the layers on the substrate which is markedly increased by contrast with the first carbon layer alone.

A method for producing a tool substrate coated with carbon in accordance with Claim 10 is likewise the subject matter

of the invention.

The essential process parameters for applying carbon layers with a high fraction of carbon in a diamond crystal structure are known. These include the feeding of a carbon carrier gas such as methane, and the feeding of molecular hydrogen, the setting of a suitable substrate temperature and the coating period over which, first and foremost, the thickness of the carbon layers is set.

10

The process conditions for applying the first carbon layer for a fraction of carbon with a diamond crystal structure which is as high as possible are preferably optimized in step a). This produces the known diamond coatings for components which exhibit excellent wear resistance.

15

In step b), the process conditions of step a) are preferably changed in order to reduce the fraction of carbon with a diamond crystal structure by contrast with the first layer.

20

This can advantageously be performed by reducing the substrate temperature in step b) by comparison with step a). Moreover, in step b) the fraction of the carbon carrier gas used can also be increased by contrast with step a), as a result of which the conditions for producing a carbon layer with a high fraction of carbon with a diamond crystal structure are "worsened".

25

The two measures named for changing the process conditions from step a) to step b) can be taken individually or else in combination with one another.

30

In the case of the CVD process used, in particular the hot-filament CVD process, it is also possible in step b) as contrasted with step a) to increase the distance of the substrate from the gas excitation, or to reduce the supply

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- 10 -

of power for the gas excitation. The introduction of extraneous gases likewise leads in most cases to a reduction in the fraction of carbon with a diamond crystal structure. An exception is formed by oxidizing gases which can also  
5 lead to an increase in diamond, and can thus be used to support the production of the first carbon layer. The flow of the process gases, and the pressure in the coating facility can also be set to differ from their ideal values, which are typically present in step a), in order to achieve  
10 the process conditions for step b).

The invention is explained by way of example in yet more detail below with the aid of the figures, in which:

15 Figure 1 shows a diagrammatic cross sectional view of a section of a coated component;

Figure 2 shows an exemplary Raman spectrum illustrating the diamond value;

20

Figure 3 shows a Raman spectrum of the first carbon layer of the component of Figure 1;

25 Figure 4 shows a Raman spectrum of the second layer of the component of Figure 1;

Figure 5 shows an electron microscope image of a cross section, produced by means of a fracture, of an edge in the case of the component of Figure 1 at  
30 an approximately 1,500-fold magnification;

Figure 6 shows a detail from Figure 5 at an approximately 6,500-fold magnification; and

35 Figure 7 shows an electron microscope image of the outer

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surface of the second carbon layer of the component of Figure 1, at an approximate 6,500-fold magnification; and

- 5 Figure 8 shows, for comparison with Figure 7, a surface of a carbon layer produced in accordance with a conventional CVD diamond coating method, at an approximately 6,500-fold magnification.
- 10 The first step is to describe an exemplary process with the aid of which a component can be produced which has two carbon layers A, B differing from one another in their fraction of carbon with a diamond crystal structure (compare Figure 1).
- 15 The process is a so-called hot-filament process.

In order to pretreat a substrate with 6% Co by weight, remainder tungsten carbide with an average grain size of 1.5  $\mu\text{m}$ , etching is initially performed for 10 minutes in 10%  
20 strength nitric acid at room temperature, after which the substrate surface was seeded for 3 minutes in a suspension of 200 ml distilled water and 8 carat diamond powder with an average grain size of 5  $\mu\text{m}$ .

The further process is carried out in a multi-filament coating apparatus, in which one or more substrates are arranged  
25 between two planes of heating elements aligned parallel to one another, the planes also lying parallel to one another. The essential parameters for carrying out a process for producing a diamond-coated tool are pressure in the coating  
30 apparatus, fractions of the process gases of hydrogen and methane in the atmosphere in the coating apparatus, total gas flow per litre of volume of the coating apparatus, substrate heating element temperature, spacing between substrate and heating element and coating time.

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The following Tables 1 and 2 specify the setting values for the parameters, Table 1 relating to the process conditions for the first carbon layer A, and Table 2 relating to the process conditions of the second carbon layer B.

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Table 1:  
Parameters for applying layer A

Parameter	Value
Pressure	20 hPa
Gas1 H <sub>2</sub>	99 Vol. %
Gas2 CH <sub>4</sub>	1 Vol. %
Total gas flow per litre of chamber volume	25 ml <sub>n</sub> /min/l
Substrate temperature	850°C
Heating element temperature	2000°C
Spacing between substrate and heating element	10 mm
Time	12 h
Layer thickness achieved	ca. 4 µm
Diamond value K <sub>A</sub> achieved	ca. 5

Table 2:  
Parameters for applying layer B

Parameter	Value
Pressure	20 hPa
Gas1 H <sub>2</sub>	98.2 Vol. %
Gas2 CH <sub>4</sub>	1.8 Vol. %
Total gas flow per litre of chamber volume	25 ml <sub>n</sub> /min/l
Substrate temperature	800°C
Heating element temperature	1910°C
Spacing between substrate and heating element	10 mm
Time	12 h
Layer thickness achieved	ca. 3 µm
Diamond value K <sub>B</sub> achieved	ca. 0.9

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A comparison of Tables 1 and 2 shows that, by contrast with the step a), for the step b) the heating element temperature, and thus the substrate temperature are lowered, and the fraction of the methane process gas is increased. The result of this is that the fraction of carbon with a diamond crystal structure in the second carbon layer is reduced, fractions of carbon with a graphite crystal structure and amorphous structure increasing correspondingly.

Tables 1 and 2 also give the so-called diamond value  $K_A$  or  $K_B$ , which relates to the fraction of carbon in the relevant carbon layer A or B with the diamond crystal structure. In general, the diamond value increases with an increasing fraction of carbon with a diamond crystal structure in the carbon layer. The determination of the diamond value is explained below with the aid of Figure 2.

Figure 2 shows an exemplary so-called micro-Raman spectrum. Such micro-Raman spectra can be measured when laser light is irradiated onto the carbon layers A, B of the component illustrated in Figure 1. The shape of the micro-Raman spectrum is determined by the structure, illustrated in Figure 1, of a component, produced in accordance with the previously described process, having the substrate M, the first carbon layer A, applied directly on the substrate M, and the carbon layer B adjoining the first carbon layer A.

The green exciting wavelength of an argon-ion laser at 514 nm was used consistently. The spectra can be taken both after applying the layer A or B to the surface, and in the fracture or polished section from the side when the entire coating process is finished.

The dependence of the Raman scattered light intensity on the wavenumber ( $\text{cm}^{-1}$ ) as illustrated in Figure 2 exhibits in the



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region of the wavenumber  $1332\text{ cm}^{-1}$  a peak of small linewidth which is to be ascribed to  $\text{sp}^3$ -bound crystalline carbon as diamond. This peak, denoted herebelow as S, is representative of the structure of the carbon as a diamond crystal structure with long-range order. The peak S is produced by the excitation of the three-fold degenerate  $\text{T}_{2g}$ -phonon mode (the point group  $\text{O}_h$  according to the group theory).

Furthermore, the Raman spectrum of Figure 2 exhibits at  $1560\text{ cm}^{-1}$  a further peak, denoted here as F, with a substantially greater linewidth by comparison with S. The peak F originates from phases of the carbon which exhibit no diamond crystal structure, for example graphitic or amorphous phases. The peak F originates chiefly from the Raman scattered light denoted as G-band in the specialist literature. The G-band is produced by the excitation of the  $\text{E}_{2g}$ -mode (the point group  $\text{D}_{6h}$  according to the group theory) of the crystalline graphite, although line broadening owing to amorphous and other additional phases of the carbon is to be observed.

The ratio  $K_A$  (first carbon layer) or  $K_B$  (second carbon layer) of the peak heights S to F after subtraction of the broad background is now determined as a measure of the diamond fraction in the carbon layers, that is to say

$$K_A = I(S_A)/I(F_A),$$

$$K_B = I(S_B)/I(F_B), \text{ respectively.}$$

The background contains a so-called D-band and scattered light which depends on the specific measuring set-up and on the other effects such as Rayleigh scattering and fluorescence radiation. The subtraction of the background for the peak S in accordance with Figure 2 is undertaken by defining a point P1 and a point P2 respectively on the shortwave and

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longwave sides of the peak S. The height of the peak S is yielded from the difference between the intensity values for the peak maximum in the region of the wavenumber  $1332\text{ cm}^{-1}$  and the intensity of the background for the same wavenumber, a straight line which connects the points P1 and P2 being used to estimate the intensity of the background.

Similarly, the background for the peak F is yielded from a straight line connecting the point P2 and a point P3 which are arranged on the shortwave side of the peak F.

Further peaks can also occur in special cases, but they are not relevant if they are outside the wavenumber interval of  $1200\text{--}1700\text{ cm}^{-1}$ , or their magnitude is less than the peak height of the peaks S and F. For example, at  $1150\text{ cm}^{-1}$ , in certain instances a peak can be observed which is to be ascribed to nano-crystalline diamonds. Nano-crystalline diamond is surrounded by carbon of non-diamond structure. Therefore, the presence of nano-crystalline diamond in the second carbon layer is advantageous because the carbon with non-diamond structure around the nano-crystalline diamonds increases the thermal expansion coefficient of the second carbon layer.

A peak occurring at  $1355\text{ cm}^{-1}$  (so-called D-band) is likewise Raman scattered light which is, however, generated by violating the selection rules for the Raman scattering on the basis of increased focal surface scattering. The D-band is greatly widened and is eliminated by the background correction described above.

The diamond value  $K_A$  or  $K_B$  serves for identifying the first and the second carbon layer, and is associated with the actual diamond fraction only to the extent that there is a strict monotonic dependence in the mathematical sense.

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The fraction of diamond is substantially higher than the relative peak heights of S and F indicate. According to Zhu, W. et al., "Characterization of diamond films on binderless W.-Mo composite carbide", in Diamond and Related Materials, 3 (1994) pages 1270-1276 and other references, the scattering intensity of the peak for diamond turns out to be approximately 50-100 times weaker than for the other phases. That is to say, given the presence of an S peak it is to be assumed that there is a greatly predominant fraction of diamond in the layer.

Even such small deviations between the first and second carbon layers lead to substantial advantages with regard to the adhesive strength of the carbon layer as a whole on the substrate. The diamond value is 1.45 in the example of Figure 2.

Figure 3 is a micro-Raman spectrum of the first carbon layer with a high fraction of  $sp^3$ -bound carbon with long-range order. The peak F is very low, while the peak S is prominent. An evaluation of the Raman spectrum leads to a diamond value of 5.3.

Particularly informative micro-Raman spectra can be obtained for the carbon layers A and B when the diamond-coated component which is to be investigated is fractured or polished to produce a cross section. The Raman spectra can then be recorded on the basis of the face of the fracture or polished section. The appearance of a fracture face is illustrated below with the aid of Figures 5 and 6.

Figure 4 reproduces a micro-Raman spectrum of the second carbon layer for the component. The relationships are inverted by comparison with Figure 3 as regards the peaks S and F. A diamond value of 0.85 is yielded.

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Figures 5 and 6 show the layer system on the component as an electron microscope photograph of an artificially engineered fracture, Figure 6 illustrating an external section of Figure 5. The carbon layers A and B and the substrate M are  
5 respectively illustrated.

The different surface structure of the second carbon layer B (Figure 7) by comparison with the surface structure of a conventionally produced CVD diamond coating is explained  
10 with the aid of Figures 7 and 8. The higher fraction of amorphous phases in the case of a surface illustrated in Figure 7 can be detected straight away.

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## Claims

1. Coated tool, in particular for machining, having a substrate, which has a predetermined coefficient of thermal expansion, and a first carbon layer which is deposited on the substrate, which has a predetermined fraction of carbon with a diamond crystal structure and a coefficient of thermal expansion which is smaller than the coefficient of thermal expansion of the substrate, characterized in that provision is made of at least one second carbon layer (B), which is deposited further outside with reference to the substrate (M) than the first carbon layer (A), and in the case of which the fraction of carbon with a diamond crystal structure is lower than the predetermined fraction of carbon with a crystal diamond structure in the first carbon layer (A), and in the case of which the coefficient of thermal expansion is greater than the coefficient of thermal expansion of the first carbon layer (A).
2. Tool according to Claim 1, characterized in that the second carbon layer (B) is deposited directly on the first carbon layer (A).
3. Tool according to Claim 1, characterized in that formed between the first carbon layer (A) and the second carbon layer (B) is an interlayer in the case of which the fraction of carbon with a diamond crystal structure drops continuously from the first carbon layer (A) in the direction of the second carbon layer (B).
4. Tool according to one of Claims 1 to 3, characterized in that it has an overall thickness of the first carbon layer (A) and the second carbon layer (B) in the range

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from 1 to 40  $\mu\text{m}$ .

5. Tool according to Claim 4, characterized in that it has an overall thickness of the first carbon layer (A) and the second carbon layer (B) in the range of 4 to 20  $\mu\text{m}$ .
6. Tool according to Claim 5, characterized in that an overall thickness of the first carbon layer (A) and of the second carbon layer (B) in the range of 6 to 15  $\mu\text{m}$  is formed.
7. Tool according to one of Claims 1 to 6, characterized in that the ratio of the thickness of the first carbon layer (A) to the thickness of the second carbon layer (B) is in the range of 0.05 to 0.9.
8. Tool according to Claim 7, characterized in that the ratio of the thickness of the first carbon layer (A) to the thickness of the second carbon layer (B) is in the range of 0.1 to 0.5.
9. Tool according to one of Claims 1 to 8, characterized in that the second carbon layer (B) has a minimum thickness of 0.5  $\mu\text{m}$ .
10. Tool according to one of claims 1 to 9, characterized in that the second carbon layer (B) consists of nanocrystalline diamond.
11. Process for producing a tool substrate which is coated with carbon and has a predetermined coefficient of thermal expansion, having the following steps:
  - a) depositing onto the tool substrate (M) a first carbon layer (A), the process conditions being

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selected such that the carbon layer (A) contains a predetermined fraction of carbon with a diamond crystal structure and has a smaller coefficient of thermal expansion than the tool substrate (M); and

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- b) depositing a second carbon layer (B), which lies further outside with reference to the substrate (M) than the first carbon layer (A), the process conditions being selected in such a way that by contrast with the predetermined fraction of carbon with a diamond crystal structure of the first carbon layer (A) the second carbon layer (B) has a reduced proportion of carbon with a diamond crystal structure and a larger coefficient of thermal expansion than the first carbon layer (A).

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12. Process according to Claim 11, in which in step a) the process conditions are selected such that the first carbon layer (A) has as high as possible a fraction of carbon with diamond crystal structure.

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13. Process according to Claim 11 or 12, in which in step b) the process conditions of step a) are changed to reduce the fraction of carbon with a diamond crystal structure by comparison with the first carbon layer (A).

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14. Process according to Claim 13, in which in step b) the substrate temperature is reduced by comparison with step a).

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15. Process according to one of Claims 13 or 14, in which in step b) the proportion of carbon carrier gas used is increased by comparison with step a).

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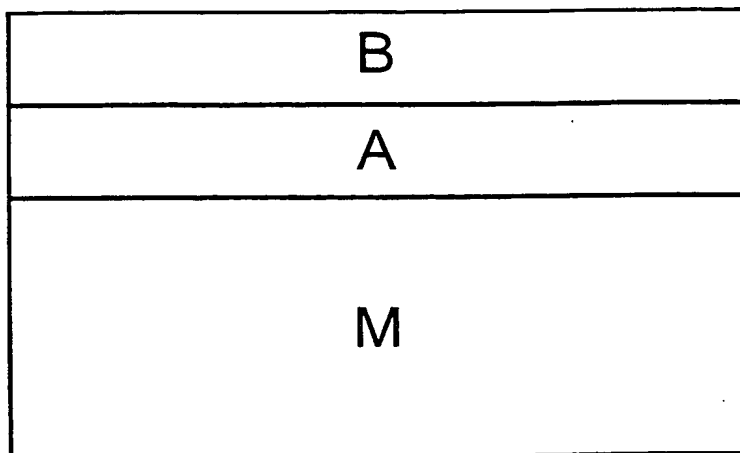


Fig.1

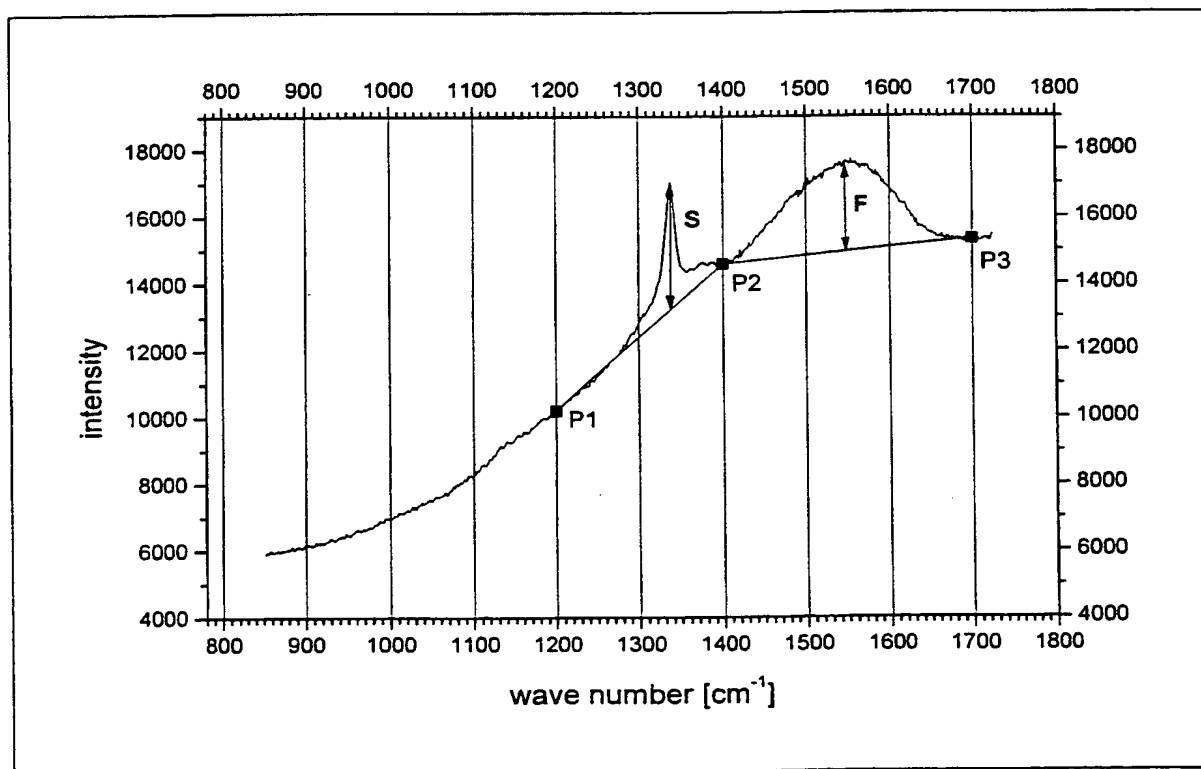


Fig.2

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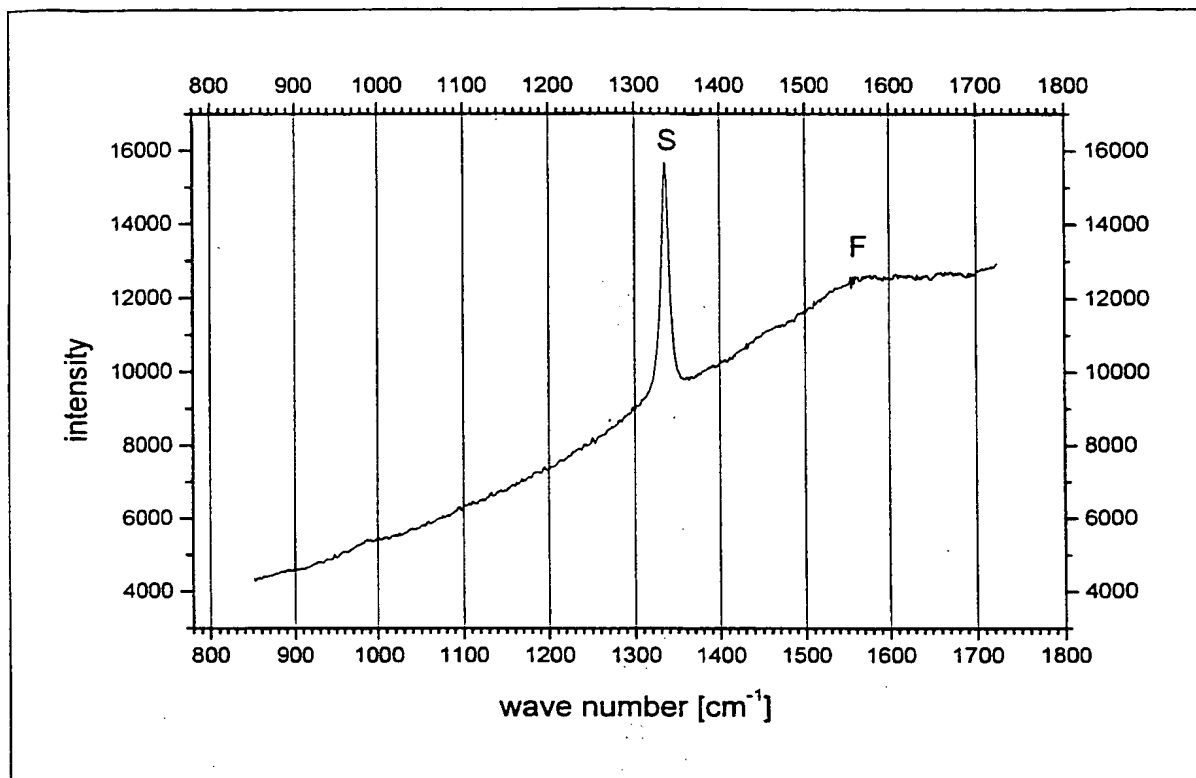


Fig.3

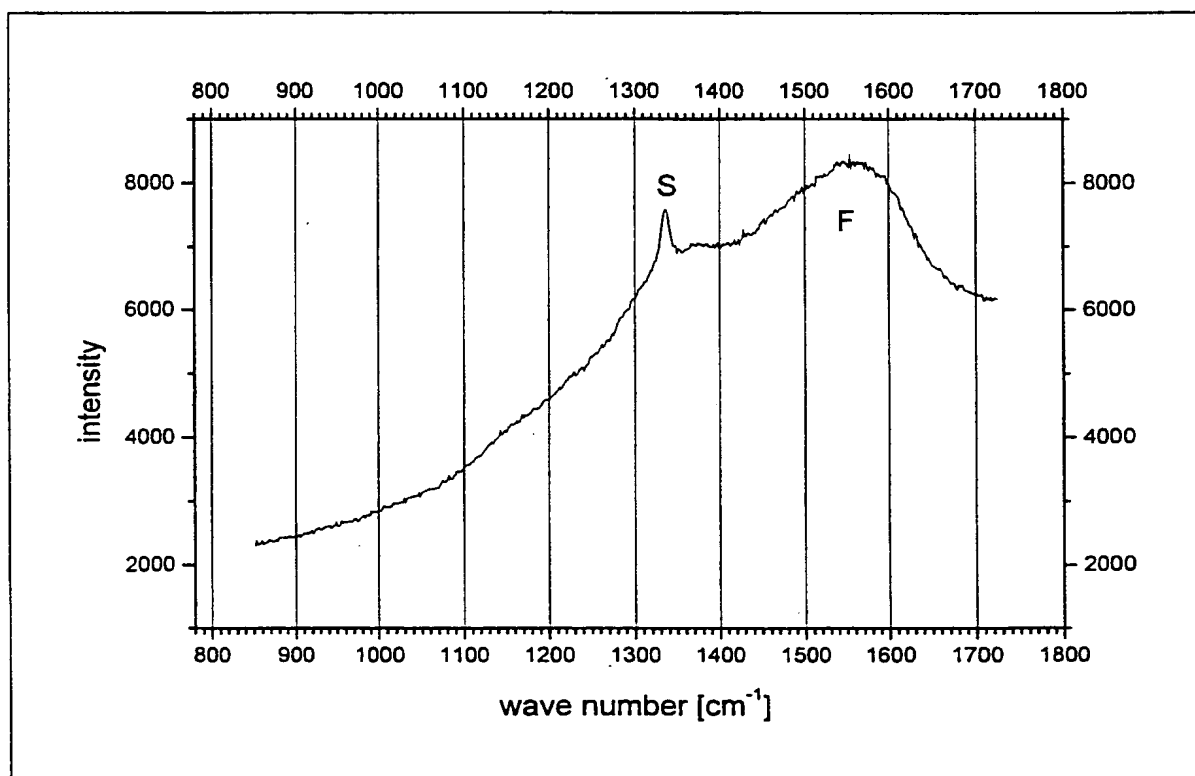


Fig.4

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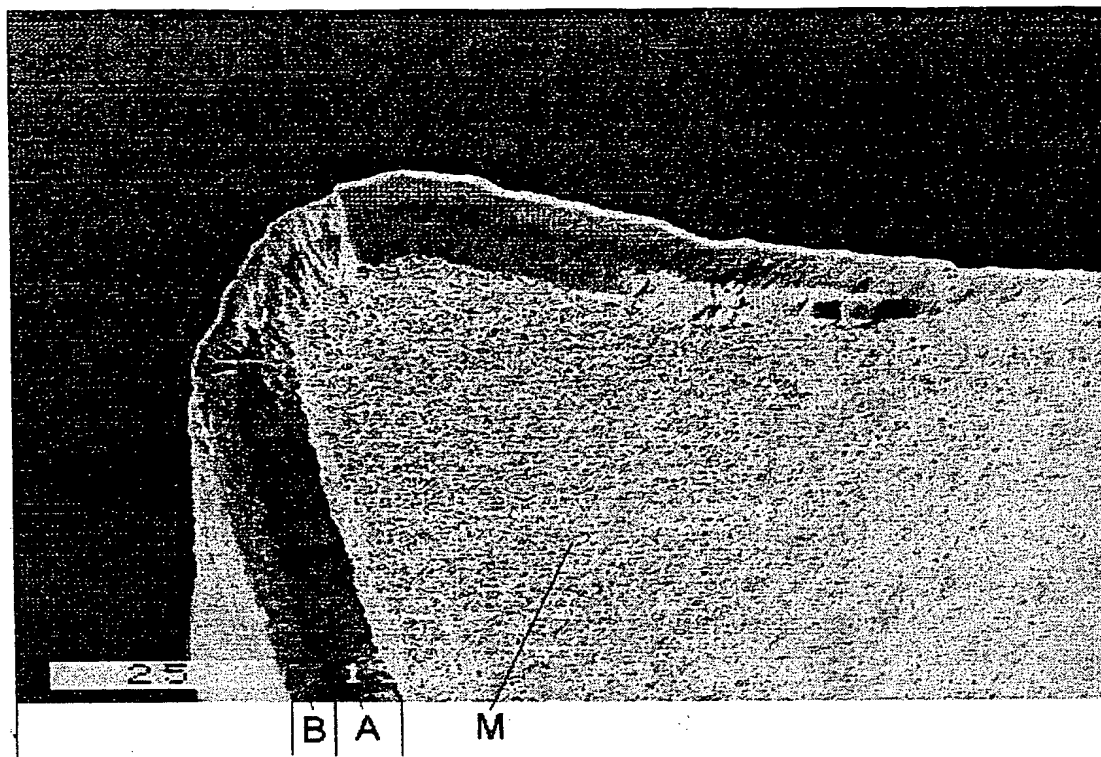


Fig.5

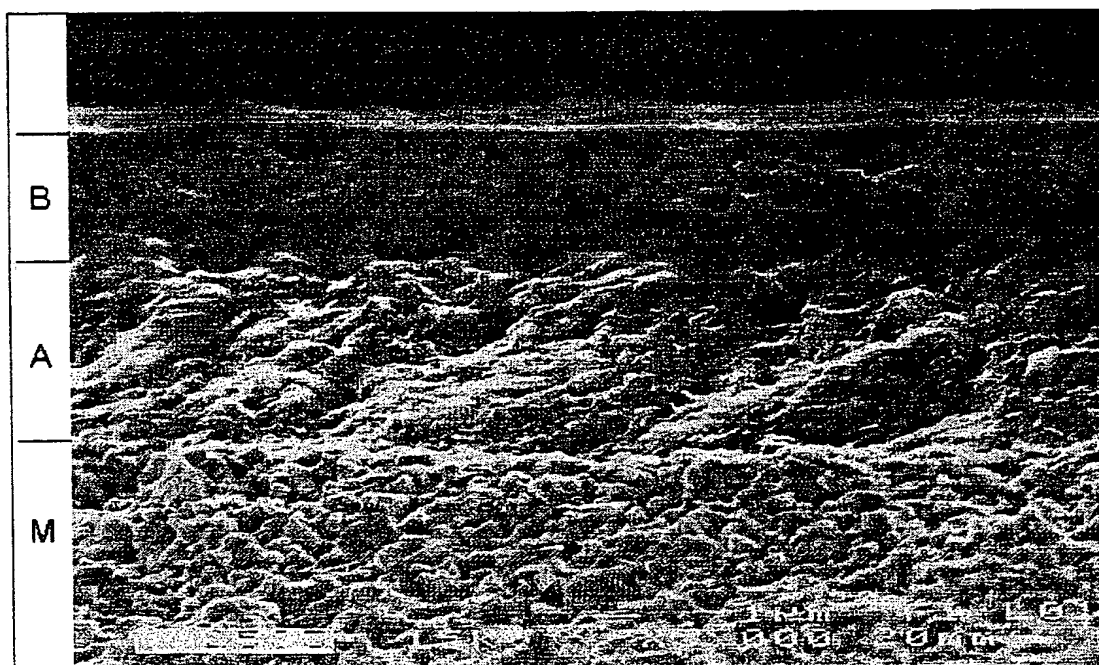


Fig.6

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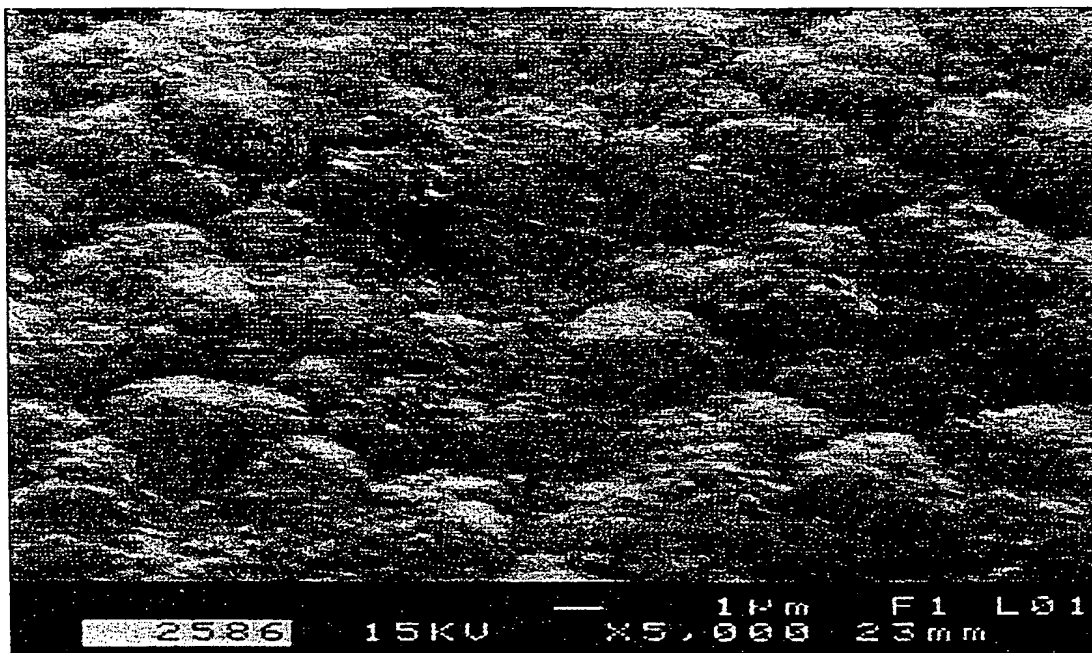


Fig.7



Fig.8

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# INTERNATIONAL RESEARCH REPORT

Internationales Aktenzeichen:  
PCT/EP 00/02890

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES  
C23C28/04, B23B27/20

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK <sup>7</sup>

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Recherchierte Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)  
B23B, B23Q, C04B, C23C

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Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

## C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	EP 0596619 A (CRYSTALLUME) 11 May 1994, the whole document. --	1-15
A	DATABASE WPI Week 199310 Derwent Publications Ltd., London, GB; Class B23B, AN 1993-079840 & JP 05 023903 A (MITSUBISHI MATERIALS CORP.) 02 February 1993, abstract. --	1-15
A	DATABASE WPI Week 199239 Derwent Publications Ltd., London, GB; Class B23B,	1-15

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

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**ANNEX**

To the International Search Report to the international Patent Application No.

PCT/EP 00/02890 SAE 278731

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

**ANNEXE**

Au rapport de recherche international relatif à la demande de brevet international n°

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

Im Recherchenbericht angeführte Patentedokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche			Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
EP	A1	596619	11-05-1994		CA	AA	2102159	04-05-1994
					JP	A2	6316764	15-11-1994
JP	A2	5023903	02-02-1993				none	
JP	A2	4223806	13-08-1992				none	